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EMISSION BANDS OF THE PO MOLECULE*

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(Plate VIII)

ABSTRACT. In the course of an investigation on the bands of the P_2 molecule, excited under different conditions, the characteristic bands, ascribed by previous investigators to the PO molecule, in the region λ 2600 and λ 3300, are found to be strongly emitted in a wide open heavy current arc between graphite poles containing phosphorus pentoxide. The bands at λ 3300, which are not yet analysed, are partly red and violet degraded. Several attempts to include all the heads into one system having failed, the red-degraded bands are analysed into one vibrational system and the violet-degraded bands into another system, suggested to be due respectively to the electronic transitions $^2\Sigma - ^2\Pi$ and $^2\Pi - ^2\Pi$ with a common lower $^2\Pi$ state, same as the ground $^2\Pi$ state of λ 2600 system, established by Ghosh and Ball and by Sen Gupta.

INTRODUCTION

Band spectra of the diatomic oxide molecules of Group V-b elements have been extensively studied and our knowledge of these has been much extended in recent years (Connelly, 1934; Sen Gupta, 1939, 1944, 1945). Four systems (γ, β, δ and ε) are analysed in NO, one in PO, two systems (A and B) in AsO, three (A, B and C) in SbO, and one in BiO molecule. In all these homologous molecules it has been suggested that the lower ground state is a $^2\Pi$ and the upper is either a $^2\Sigma$ or a $^2\Pi$, giving rise to doublet systems of bands with the $^2\Pi$ interval, increasing from 121 cm^{-1} for NO to 2272 cm^{-1} for SbO. Although the main features of these spectra are known, it is obvious that for a complete correlation there is need for further investigation, particularly of the bands of the oxides of phosphorus and of bismuth.

The early work on the PO bands was summarised by Petrikaln (1928) who investigated these bands in emission and in absorption and reported the existence of two characteristic systems for this molecule, one at λ 2600 and another in the region λ 3300. Ghosh and Ball (1931), however, were the first to report a complete vibrational analysis of the more refrangible of these two systems. It was shown to consist of double double-headed bands analogous to the γ bands of nitric oxide, with well-marked sequences and represented by the vibrational constants,

$\nu_e = 40264.7\ cm^{-1}$	$\omega' = 1391.0$	$x'\omega' = 7.65$
$40488.5\ cm^{-1}$	$\omega'' = 1230.6$	$x''\omega'' = 6.52$

The rotational structure was investigated by Sen Gupta (1935) who established the electronic transition of this system as $^2\Sigma - ^2\Pi_i$ with the $^2\Pi$ interval

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equal to 224 cm^{-1}. But the less refrangible system at λ 3300 remained as yet unanalysed. Curry, Herzberg and Herzberg (1933) recorded the following molecular constants,

$$\nu_0 = 30584, \qquad \omega_0' = 1151, \qquad \omega_0'' = 1228,$$

but no detailed analysis has, as far as the authors are aware, been published till now. Even the published wave-length data of the bands does not appear to be definite; the measurements made by Petrikaln do not correspond well with those by Geuter. In view of this and the peculiar appearance of the bands a study of this system was undertaken.

EXPERIMENTAL

The experimental work on the bands formed part of an earlier investigation on the P_2 bands (N. Rao, 1943) in the course of which several different sources of exciting the bands were utilised. The PO bands were found to be strongly emitted in a wide-open heavy current arc between carbon electrodes fed by phosphorus pentoxide and absent altogether in the ordinary transformer discharge through P_2O_5, which only gave bands due to oxygen, phosphorus and CO or NO. The arc consisted of a lower positive graphite electrode about 1.5 cm. in diameter in which a cylindrical hole 10 mm. × 7 mm. was drilled, and the phosphorus pentoxide powder transferred directly into it. The upper graphite electrode was about 6 mm. in diameter. The arc fed by a current of 7 to 8 amperes was drawn out into a long flame, the central portion of which was focussed on the slit of the spectrograph. Preliminary photographs before introducing P_2O_5, taken with the graphite rods alone under identical conditions, served as comparision spectra. A well-developed band system was obtained in the region from λ 3580 to λ 3150, the most peculiar feature of which is that some of the bands were degraded to the red and others to the violet. This feature was recorded also by Petrikaln who photographed the bands in absorption using specially prepared phosphorus trioxide.

Plate VIII is a reproduction of the spectra obtained with a Hilger quartz Littrow spectrograph type E_1, with and without phosphorus pentoxide in the electrodes and iron arc comparison. The exposure was for about half-an-hour.

The wavelengths of all the band heads in order are recorded in Table I; they closely agree with the published measurements due to Geuter. The letter V or R in the last column indicates the direction of degradation (violet or red) of the band.

ANALYSIS

As mentioned earlier, each of the diatomic oxide molecules, homologous with PO, gives band systems due to transitions into a $^2\Pi$ state from one or more upper states which may be either a $^2\Sigma$ or a $^2\Pi$. The PO bands under

TABLE I

Bands of PO molecule

Wave length	Intensity	Wave number	Classification	
			Violet-degraded system	Red-degraded system
3579.4	1	27930	V (3, 5)	
3578.6	1	27936	V	
3567 9	1	28019	V (2. 4)	
3563 2	1	28057	V	
3562 6	1	28061	V	
3550.2	0	28159	V (0, 2)	
3542 6	1	28220	V	
3541.9	1	28225	V	
3539 0	1	28249	V (2, 4)	
3530.1	0	28320	V (1, 3)	
3521.2	1	28391	V (0, 2)	
3478.6	1	28739		R
3470 8	1	28804		R (3, 4)
3460 1	2	28893		R (1, 2) ?
3450 9	1	28969		R (0, 1)
3442.4	1	29041		R
3431.7	1	29132		R (1, 2)?
3424.4	3	29194	V (2, 3)	
3413.9	3	29284	V (1, 2)	
3409.7	3	29320	V (3, 4)	
3405 7	3	29354	V (0, 1)	
3397.8	3	29422	V (2, 3)	
3396.4	2	29435	V	
3387.8	3	29509	V (1, 2)	
3386.3	2	29522	V	
3379.8	3	29579	V (0, 1)	
3366.1	3	19647		R
3362.5	2	29731		R (4, 4)
3360.8	2	29746		R (4, 4)
3346.3	3	29875		R (2, 2)
3340 7	2	29925		R (3, 3)
3339.7	2	29934		R (3, 3)
3328.4	3	30036		R (1, 1)
3321.0	3	30103		R (2,2)
3319.8	2	30114		R (2, 2)
3312.0	3	30185		R (0, 0)
3303.2	2	30265		R (1, 1)
3301.1	2	30284		R (1, 1)
3296.5	3	30327		R (10, 8)
3286.0	3	30423		R (0, 0)
3280,4	1	30475		R (5, 4)
3270.4	2	30569	V (0, 0)	
3269.3	2	30579		R (10, 8)
3266.8	1	30602	V (2, 2)	
3255.2	2	30711	V (1, 1)	
3253.6	2	30726		R (4, 3)
3246.2	3	30796	V (0, 0)	
3238.6	1	30869		R (3, 2)
3217.4	1	31027		R (2, 1)
3204.3	1	31199		R (7, 5)
3198.9	1	31252		R (1, 0)
3198.2	1	31259		
3188.2	2	31357		R (6, 4)
3180.7	2	31431		R (7, 5)
3173.4	2	31503		R (1, 0)
3164.9	1	31587		R (6, 4)
3149.8	2	31739		R (9, 6)

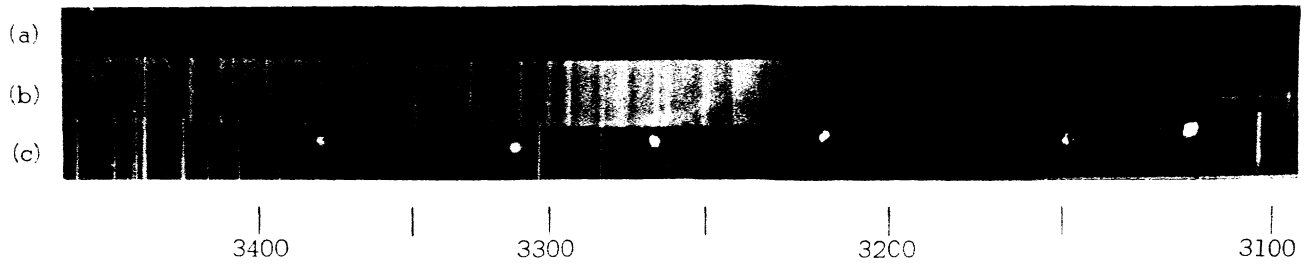
investigation may be expected to be due to a similar electronic transition. If they all belong to one system, say $^2\Sigma - {}^2\Pi$, they must consist of double double-headed bands with the doublet width equal to 224 cms^{-1}. Examination of the bands has, no doubt, revealed several heads with the wave-number intervals either equal to or not far from the value of 224 cms^{-1}. But not all the component heads show the doublet structure: some of these are close doublets and others are not. This has led to the suspicion that the bands under investigation may comprise of two overlapping systems. Another peculiar feature leading to the same view is that some of the bands are red-degraded (mostly those which show close doublet structure) and others are violet-degraded, although instances are known of band systems where, in one and the same system, there is a change in the direction of degradation of the bands. The previous investigators, *e.g.* Petrikaln, as also Curry, Herzberg and Herzberg seem to have attempted the analysis of the PO bands on the supposition that there is only one system and the latter authors have suggested a possible $^2\Pi - {}^2\Pi$ transition. The first attempts of the authors were to examine the possibility of including all the band heads into one and the same system either a $^2\Sigma - {}^2\Pi$ or a $^2\Pi - {}^2\Pi$ (the latter transition possibly giving rise to single-headed bands). The constants recorded by Curry, Herzberg and Herzberg were also considered and on the basis of these values the possibility of fitting all the bands into one system was studied. All these attempts having failed, recourse was taken to the alternative possibility of regarding the bands as belonging to two overlapping systems. The analysis thus arrived at is shown in Tables II and III.

TABLE II

Vibrational Analysis of the PO Bands. (Red-degraded system.) (System A.)

		0	1	2	3	4	5
0	Q	30423(3)					
	Q	30185(3)	28969(1)				
1	R	...	30284(2)				
	Q	31503(2)	30265(3)				
	Q	31252(1)	30036(3)				
2	R		...	30114(1)			
	Q		...	30103(3)			
	Q		31072(1)	29875(3)			
3	R			...	29934(2)		
	Q			...	29925(2)	28804(1)	
	Q			30869(1)	...	...	
4	R				...	29746(2)	
	Q				...	29731(2)	
	Q				30726(2)	...	
5	Q					...	
	Q					30475(1)	
6	Q					31587(1)	
	Q					31557(2)	
7	Q						31431(2)
	Q						31499(1)

(a) Iron Arc (b) P_2O_5 in Carbon Arc showing PO bands (c) Carbon Arc



PO Bands

TABLE III

Vibrational Analysis of the PO Bands. (Violet-degraded system.) (System B.)

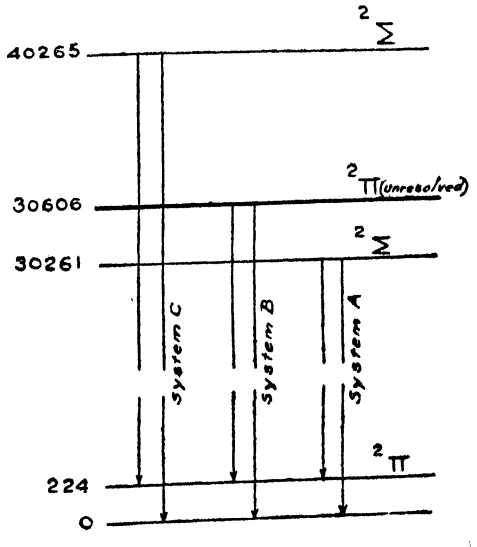
	0	1	2	3	4	5
0	30569(2) 30796(3)	29354(3) 29579(3)	28159(0) 28391(1)			
1		... 30711(2)	29284(3) 29509(3)	28320(0)		
2			... 30602(1)	29194(3) 29422(3)	28019(1) 28249(1)	
2					... 29320(3)	27930(1) ...

All the red-degraded bands form one system. The Q head interval is nearly 224 cms^{-1} and in most cases the component R heads are also detected. The electronic transition is probably $^2\Sigma - {}^2\Pi$. The bands are approximately represented by the formula

$$\nu = 30260.8 + [1094(v' + \tfrac{1}{2}) - 14.5(v'' + \tfrac{1}{2})^2] - [1234(v'' + \tfrac{1}{2}) - 9.5(v'' + \tfrac{1}{2})^2]$$

The violet-degraded bands are all arranged into a second system. The bands are single-headed. They are perhaps due to the transition $^2\Pi - {}^2\Pi$ and may be represented approximately by the formula

$$\nu = 30606.5 + [1151.9(v' + \tfrac{1}{2}) - 14.2(v' + \tfrac{1}{2})^2] - [1224.(v'' + \tfrac{1}{2}) - 6.5(v'' + \tfrac{1}{2})^2]$$



Electronic transitions in PO bands.

FIG. 1

If the analysis proves correct, an interesting feature of this system, which deserves mention, is that while the bands themselves are degraded to the violet, the sequence degradation is towards the red.

The lower state for these two band systems is considered to be identical with the lower state of the most refrangible system which was analysed by Ghosh and Ball. There are thus three identified systems among the PO bands which may be designated as A, B, and C, in the order of diminishing wavelength and the electronic transitions concerned, may be represented diagramatically as in the Fig. 1.

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